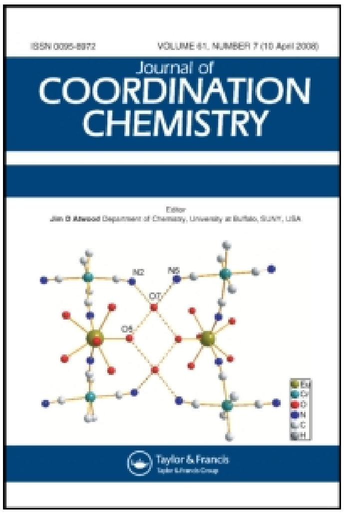

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The synthesis and characterization of *N*-{2-[(1,4-dioxaspiro[4.5]- dec-2-ylmethyl)amino]ethyl}-*N*'-hydroxy-2-(hydroxyimino)ethanimidamide and some of its transition metal complexes

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THE SYNTHESIS AND CHARACTERIZATION OF *N*-{2-[(1,4-DIOXASPIRO[4.5]-DEC-2-YLMETHYL)AMINO]ETHYL}-*N′*-HYDROXY-2-(HYDROXYIMINO)ETHANIMIDAMIDE AND SOME OF ITS TRANSITION METAL COMPLEXES

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A new soluble *vic*-dioxime, *N*-{2-[(1,4-dioxaspiro[4.5]dec-2-ylmethyl)amino]ethyl}-*N′*-hydroxy-2-(hydroxyimino)ethanimidamide (**LH_2**) has been synthesized and mononuclear complexes have been obtained with Co(II), Ni(II), Cu(II) and Zn(II) salts. Different types of metal complexes, such as $[Co(LH)_2(H_2O)_2]$, $[M(LH)_2]$ (M = Ni(II) and Cu(II)) and $[Zn(LH)(Cl)(H_2O)]$, were obtained. Co(II), Ni(II) and Cu(II) form complexes with LH_2 which have a metal ligand ratio of 1 : 2. Zn(II) forms a complex with H_2L which has a metal–ligand ratio of 1 : 1. Structures of these compounds were identified by using elemental analyses, IR, ^1H and ^{13}C NMR spectra, electronic spectra, magnetic susceptibility measurements, conductivity measurements and thermogravimetric analyses (TGA).

Keywords: *vic*-Dioxime; Transition metal complexes; Cobalt(II); Nickel(II); Copper(II); Zinc(II)

INTRODUCTION

As important ligands in coordination chemistry, *vic*-dioximes and their metal complexes have been investigated for a long time [1–6]. These ligands and their metal complexes have played a significant role in the domains of stereochemistry, structure, spectroscopy, catalysis, models for biological systems, polymers, pigments and dyes as well as organic, analytical, inorganic, medical and industrial chemistry [7]. *vic*-Dioximes and monooximes are amphoteric materials containing weak acidic–OH groups and basic C=N groups. The geometrical isomers of *vic*-dioximes and their derivatives, depending on the position of the OH groups in the molecule, are *syn*, *anti* and *amphi* structures; usually, the stability order of these is anti > amphi > syn configuration [8], but there are some exceptions [9]. The *anti* and *amphi* forms of these isomers give two differently colored complexes with the same metal but the syn

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form does not form complexes [10]. Among the three isomers, the *anti* is more liable to form N,N-coordinated planar complexes stabilized by hydrogen bonding [11]. Compounds containing the 1,3-dioxolone group are used as solvents, additives and corrosion retardants. Polymers containing the 1,3-dioxolane groups exhibit semiconducting behavior, while some polymers and copolymers of 1,3-dioxolane exhibit herbicidal and perfume activity [12].

In previous studies we investigated the synthesis and characterization of various transition metal complexes of novel *vic*-dioximes [13–16]. In the present paper, we report the synthesis and characterization of a new *vic*-dioxime ligand and its mononuclear complexes.

EXPERIMENTAL

Materials

In our previous paper, we described the synthesis and characterization of these compounds. The preparation of *anti*-chloroglyoxime has been described previously [17]. All the reagents used were purchased from the Merck, Fluka or Sigma companies and are chemically pure.

Measurements

Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer from KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined on a Gallenkamp apparatus. Molar conductances of the *vic*-dioxime ligand and its transition metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. The metal contents of the complexes were determined with an Ati Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3 : 1) solution followed by dilution in water. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

Preparation of 2-(Chloromethyl)-1,4-dioxaspiro[4.5]decane (1)

15–20 drops of borontrifluoride etherate were added dropwise to purified cyclohexanone (8.20 g, 83.35 mmol) in carbon tetrachloride (100 cm^3) and epichlorohydrine (3.86 g, 41.67 mmol) was then added dropwise over a period of 5 h at temperature below 15–20°C. After the reaction was complete, the mixture was stirred for an additional 2 h at the same temperature. The catalyst $BF_3 \cdot OEt_2$ was then destroyed by addition of triethylamine (3 cm^3). The mixture was washed with water and dried over anhydrous potassium carbonate. The liquid products were distilled at 80–95°C and 8 mm-Hg.

Compound **1** was obtained in 10.65 g (63%) yield. IR (cm^{-1}): 745 (C–Cl), 1105 (C–O–C), 2870–2950 (C–H_{cyclo}). ^1H NMR (DMSO-d_6, ppm): 1.60–1.83 (m, 10H, CH_{cyclo}), 3.31 (m, 2H, CH_2–O), 3.50 (m, 2H, CH_2–Cl), 3.86 (m, 1H, CH–O). ^{13}C NMR (DMSO-d_6, ppm): 22.00 (CH_{cyclo}), 24.26 (CH_{cyclo}), 34.74 (CH_{cyclo}), 45.65 (–CH_2–NH), 64.99 (O–CH_2–), 72.80 (O–CH–), 105.22 (C_{ipso}).

Preparation of 2-(Chloromethyl)-1,4-dioxaspiro[4.5]decane and *N*-(1,4-Dioxaspiro[4.5]dec-2-ylmethyl)ethane-1,2-diamine (2)

Ethylenediamine (6.09 g, 100 mmol), triethylamine (2.55 g, 25 mmol) and absolute xylene (70 cm^3) were mixed in a reaction flask equipped with a $CaCl_2$ drying tube and a dropping funnel, and heated to 90°C. To this mixture was added dropwise a solution of 2-(chloromethyl)-1,4-dioxaspiro[4.5]decane (4.78 g, 25 mmol) in xylene (45 cm^3), and the mixture was refluxed for 20 h and then cooled to room temperature. The mixture was filtered and the filtrate was evaporated to remove excess ethylenediamine. The compounds were distilled at 105–110°C at 10 mm-Hg.

Compound **2** was obtained in 3.44 g (64%) yield. IR (cm^{-1}): 3380 (–NH). ^1H NMR (DMSO-d_6, ppm): 1.50–1.80 (m, 10H, CH_{cyclo}), 1.36 (s, 3H, $NH_{deuterium\ exchangeable}$), 3.10–3.74 (m, 6H, N–$CH_2$–), 3.54 (m, 2H, CH_2–O), 4.19 (m, 1H, CH–O). ^{13}C NMR (DMSO-d_6, ppm): 23.44 (CH_{cyclo}), 24.90 (CH_{cyclo}), 36.51 (CH_{cyclo}), 40.43 (–CH_2–NH), 48.47 (NH–CH_2–), 50.96 (CH–CH_2–), 68.05 (O–CH_2–), 75.43 (O–CH–), 109.32 (C_{ipso}).

Preparation of the Ligand, LH_2

A solution of $NaHCO_3$ (3.39 g, 40 mmol) was added to a solution of *N*-(1,4-dioxaspiro-[4.5]dec-2-ylmethyl)ethane-1,2-diamine (4.29 g, 20 mmol) in absolute ethanol (50 cm^2), then a solution of *anti*-chlorogyloxime (2.47 g, 20 mmol) in absolute ethanol (40 cm^3), synthesized by the method described previously [14], was added dropwise to the mixture at room temperature over 5 h, and the mixture was stirred on a water bath at 60–70°C for 10 h. The mixture was filtered and excess ethanol was removed by evaporation. The product was crystallized by addition of *n*-hexane. The obtained product was filtered off, washed with diethyl ether several times and dried in vacuum for 10 h. The purified ligand is soluble in common solvents such as EtOH, $CHCl_3$, DMSO and DMF and insoluble in diethyl ether and *n*-hexane.

Ligand $\mathbf{LH_2}$ was obtained in 3.70 g (61%) yield; m.p.: 122°C. IR (cm^{-1}): 990 (N–O), 1630 (C=N), 2870–2950 (CH_{cyclo}), 3280 (O–H), 3400 (N–H). ^1H NMR (DMSO-d_6, ppm): 1.38–1.62 (m, 10H, CH_{cyclo}), 2.94–3.46 (m, 6H, N–CH_2), 3.77–4.01 (m, 2H, CH_2–O), 4.10–4.40 (m, 1H, CH–O), 6.38 (s, 2H, N–$H_{exchangeable}$), 8.24 (s, 1H, N=C–H), 8.60 (s, 1H, N–$OH^A_{exchangeable}$), 9.15 (s, 1H, N–$OH^B_{exchangeable}$). ^{13}C NMR (DMSO-d_6, ppm): 24.43 (C_3), 25.470 (C_2–C_4), 37.50 (C_1–C_5), 41.11 (C_{11}), 49.59 (C_{10}), 51.34 (C_9), 69.46 (C_7), 76.52 (C_8), 110.93 (C_6), 148.30 (C_{12}), 150.05 (C_{13}). Anal. Calcd. for $C_{13}H_{24}N_4O_4$ (300.56) (%): C, 51.97; H, 8.07; N, 18.66. Found: C, 52.38; H, 7.70; N, 18.59.

Preparation of the Co(II), Ni(II) and Cu(II) Complexes

The ligand (0.30 g, 1 mmol) was dissolved in absolute methanol (10 cm^3). A solution of 0.5 mmol of the appropriate metal salt [$CoCl_2 \cdot 6H_2O$ (0.12 g), $NiCl_2 \cdot 6H_2O$ (0.12 g) or $CuCl_2 \cdot 2H_2O$ (0.09 g)] in absolute methanol (5 cm^3) was added dropwise to the ligand solution with continuous stirring. The color of the solution immediately turned dark brown for Co(II), tile red for Ni(II) and green for Cu(II). The pH dropped to around 3.00–3.90 and was raised to 5.5 by addition of a 1 M NaOH solution in ethanol. Each mixture was stirred for a further 1 h at 30°C. The precipitated complexes were kept on a water bath for 35 min at 40°C, filtered and the precipitate was washed with water, ethanol and diethyl ether. The complexes are soluble in acetone, EtOH, THF, DMF and DMSO and insoluble in acetonitrile, diethyl ether, *n*-hexane and benzene.

[*Co*(*LH*)$_2$(*H*$_2$*O*)$_2$] was obtained in 0.19 g (52%) yield; m.p.: 183°C. IR (cm^{-1}): 977 (N–O), 1607 (C=N), 1726 (O···H–O), 3350 (N–H), 3490 (H_2O). Anal. Calcd. for $C_{26}H_{50}CoN_8O_{10}$ (729.22) (%): C, 42.82; H, 6.93; N, 15.37; Co, 8.08. Found: C, 43.15; H, 7.29; N, 14.99; Co, 7.79.

[*Ni*(*LH*)$_2$] was obtained in 0.18 g (55%) yield; m.p.: 201°C. IR (cm^{-1}): 980 (N–O), 1603 (C=N), 1730 (O···H–O), 3375 (N–H). ^{1}H NMR (DMSO-d$_6$, ppm): 1.40–1.66 (m, 20H, CH$_{cyclo}$), 2.96–3.51 (m, 12H, N–CH$_2$), 3.83–4.03 (m, 4H, CH$_2$–O), 4.18–4.42 (m, 2H, CH–O), 6.45 (s, 4H, N–H$_{exchangeable}$), 8.41 (s, 2H, N=C–H), 16.01 (s, 2H, O···H–O$_{exchangeable}$). Anal. Calcd. for $C_{26}H_{46}NiN_8O_8$ (657.51) (%): C, 47.49; H, 7.07; N, 17.05; Ni, 8.93. Found: C, 47.83; H, 6.80; N, 16.71; Ni, 9.28.

[*Cu*(*LH*)$_2$] was obtained in 0.17 g (53%) yield; m.p.: 150°C. IR (cm^{-1}): 984 (N–O), 1610 (C=N), 1710 (O···H–O), 3370 (N–H). Anal. Calcd. for $C_{26}H_{46}CuN_8O_8$ (662.35) (%): C, 47.14; H, 7.01; N, 16.92; Cu, 9.59. Found: C, 46.77; H, 6.64; N, 17.31; Cu, 9.20.

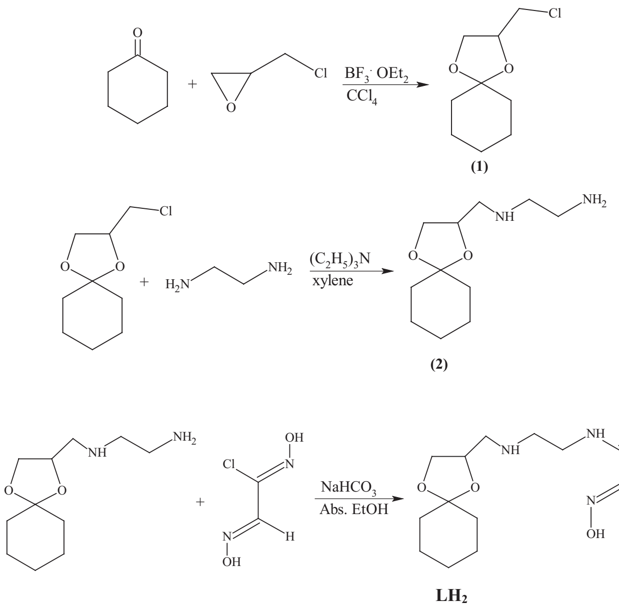
Preparation of the Zn(II) Complex

A solution of **LH$_2$** (0.30 g, 1 mmol) in absolute ethanol (45 cm^3) was added to a solution of $ZnCl_2$ (0.14 g, 1 mmol) in absolute ethanol (10 cm^3). The mixture was stirred at 60°C for 6 h. The color of the solution turned to yellow from the initial dirty white color. A yellow precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with water, ethanol and diethyl ether, and dried in vacuum. The complex is soluble in ethyl acetate, $CHCl_3$, EtOH, MeOH, THF, DMF and DMSO and insoluble in benzene, diethyl ether and *n*-hexane.

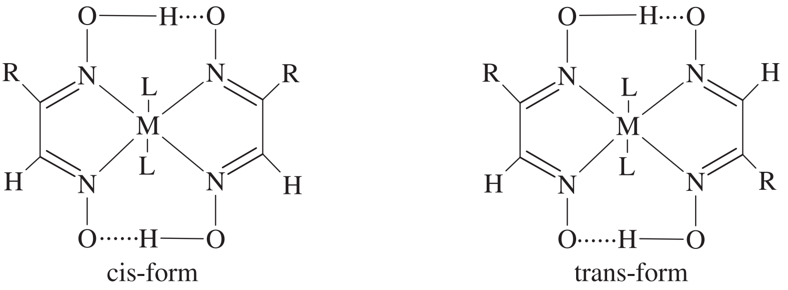
[*Zn*(*LH*)(*H*$_2$*O*)(*Cl*)] was obtained in 0.24 g (56%) yield; m.p.: 197°C. IR (cm^{-1}): 972 (N–O), 1624 (C=N), 3240 (O–H), 3397 (N–H), 3430 (H_2O). ^{1}H NMR (DMSO-d$_6$, ppm): 1.40–1.64 (m, 10H, CH$_{cyclo}$), 2.93–3.39 (m, 6H, N–CH$_2$), 3.30 (s, 2H, H_2O), 3.80–4.00 (m, 2H, CH$_2$–O), 4.13–4.40 (m, 1H, CH–O), 6.27 (s, 2H, N–H$_{exchangeable}$), 8.45 (s, 1H, N=C–H), 9.32 (s, 1H, N–OH$_{exchangeable}$). Anal. Calcd. for $C_{13}H_{25}N_4O_5Zn$ (418.26) (%): C, 37.33; H, 6.04; N, 13.40; Zn, 15.63. Found: C, 36.97; H, 5.67; N, 13.02; Zn, 16.00.

RESULTS AND DISCUSSION

The new ligand *N*-{2-[(1,4-dioxaspiro[4.5]dec-2-ylmethyl)amino]ethyl}-*N*′-hydroxy-2-(hydroxyimino)ethanimidamide (**LH$_2$**) was prepared in a three-stage process as shown in Scheme 1. The structure of **LH$_2$** was identified by elemental analysis, IR, ^{1}H and ^{13}C NMR spectra, electronic spectra, conductivity measurements and



SCHEME 1.



$R = C_{11}H_{21}N_2O_2$

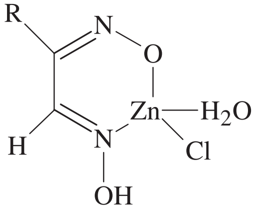
M =	Co(II)	Ni(II)	Cu(II)
L =	H_2O	-	-

FIGURE 1 Suggested structure of the octahedral and square-planar complexes of the ligand **LH_2**.

thermogravimetric analyses (TGA). The elemental analyses of the ligand and its Co(II), Ni(II) and Cu(II) complexes are in agreement with theoretical expectations. The analytical and physical data show a metal : ligand ratio of 1 : 2. The reaction of **LH_2** with Zn(II) gives a product with 1 : 1 metal : ligand ratio. Reaction of ligand and Co(II), Ni(II), Cu(II) and Zn(II) salts yield complexes corresponding to the general formulas $[Co(HL)_2(H_2O)_2]$, $[Ni(HL)_2]$ $[Cu(HL)_2]$ and $[Zn(HL)(Cl)(H_2O)]$ Figs. 1 and 2.

Infrared Spectra

In the IR spectra of the Co(II), Ni(II) and Cu(II) complexes, the absorption assigned to the $\nu(C{=}N)$ frequency in the free ligand is shifted to lower frequencies



$R = C_{11}H_{21}N_2O_2$

M =	Co(II)	Ni(II)	Cu(II)
L =	H_2O	-	-

FIGURE 2 Suggested structure of the tetrahedral complex of the ligand $\mathbf{LH_2}$.

($1603–1610\,cm^{-1}$) after complexation, owing to N,N-metal coordination [18–21]. The band observed at $990\,cm^{-1}$ in the free ligand, assigned to ν(N–O) is also shifted to lower frequency after complexation. The absorptions indicate that formation of coordination bonds is between the metal and the nitrogen atoms of the ligand. The weak bands appearing around $1710–1730\,cm^{-1}$ in the IR spectra of the complexes correspond to intramolecular hydrogen bridges (O···H–O), but these peaks are missing in the ligand [22]. For the Co(II) complex, the coordinated H_2O molecules are identified by a broad O–H absorption at $3490\,cm^{-1}$ with constant intensity after heating above 110°C for 24 h. In the IR spectrum of the Zn(II) complex, the stretching band of ν(C=N) appearing at $1630\,cm^{-1}$ in $\mathbf{LH_2}$ is shifted to $1624\,cm^{-1}$. There is no (O···H–O) peak, as expected for complexes with the formula shown in Fig. 2. At the same time, the N–O band at $990\,cm^{-1}$ in the free ligand was moved to lower frequency by *ca.* $20\,cm^{-1}$ after Zn(II) complex formation. These results suggest that the ligand is coordinated to metal ions through nitrogen and oxygen donors. A chloride ion and a water molecule are also coordinated to each metal ion. A broad band at $3430\,cm^{-1}$ was observed in the spectra of those complexes that contain coordinated water molecules [23].

^{1}H and ^{13}C NMR Spectra

In the ^{1}H NMR spectrum of $\mathbf{LH_2}$, the OH resonance appears as a singlet at 8.60–9.15 ppm (exchangeable with D_2O). A single chemical shift for the OH proton indicates that the oxime groups prevail in the *anti*-form [14–18]. Also, chemical shifts for –NH protons were observed at 6.38 ppm. These bands are easily identified by deuterium exchange [15]. The C–H protons adjacent to the oxime groups were observed at 8.24 ppm. This value is in agreement with the literature [18]. In the ^{13}C NMR spectra, the C=NOH groups in the ligand show two peaks at 148.30–150.05 ppm. These values are in good agreement with those of *vic*-dioximes. The geometric isomers of the Ni(II) complex can be inferred from the proton NMR spectrum, since the alternative chemical environments will show two O···H–O bridge protons in the *cis* form, but only one ^{1}H NMR resonance in the *trans* structure; this result can be easily supported by deuterium exchange. The observed spectrum has only one ^{1}H NMR resonance at 16.01 ppm for Ni(II), suggesting the *trans* form of the complexes [22–25]. The ^{1}H NMR spectra of the Zn(II) complex shows the presence of an N-coordinated oxime N–OH proton at 9.32 ppm and two protons of a coordinated water molecule at 3.30 ppm. The suggested structure of the complex is shown in Fig. 2 [26].

Electronic Spectra and Magnetic Properties

The electronic spectra of *vic*-dioxime ligand **(LH_2)** and its complexes were taken in DMSO, Table I. The spectra of the complexes were dominated by charge-transfer transitions in the UV-Vis region [27]. The UV-Vis spectrum of the cobalt(II) complex shows two bands at 420 and 570 nm, which may be assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. Absorptions at 354 nm are ascribed to metal-to-ligand charge transfer transitions in an octahedral complex [28]. The electronic spectra of the nickel(II) and copper(II) complexes show absorption bands at 478 and 430 nm attributed to the transitions $^1A_{1g} \rightarrow {}^1B_{1g}$ for Ni(II) and $^2T_{2g} \rightarrow {}^2E_g(G)$ for Cu(II), compatible with square-planar structures. The electronic spectrum of the Zn(II) complex shows an absorption band at 435 nm attributed to the L → M (charge-transfer) transition, which is compatible with this complex having a tetrahedral structure [29]. The UV-Vis peaks corresponding to the $\pi \rightarrow \pi^*$ transitions in the *vic*-dioxime ligand were observed at 290 nm. The peaks belonging to the $\pi \rightarrow \pi^*$ transitions are shifted to longer wavelength as a consequence of coordination, confirming the formation of *vic*-dioxime metal complexes [27].

The room-temperature solid-state magnetic moment data of the complexes are reported in Table I. Magnetic susceptibility measurements and elemental analyses results provide sufficient information to characterize the structures as shown in Figs. 1 and 2. The $[Ni(LH)_2]$ complex is diamagnetic, as expected for square-planar d^8 complexes. The $[Zn(LH)(Cl)(H_2O)]$ complex is also diamagnetic as expected for d^{10} electronic configuration, whereas the $[Co(LH)_2(H_2O)_2]$ and $[Cu(LH)_2]$ complexes are paramagnetic with magnetic susceptibility values of 4.60 and 1.68 BM, respectively [23,30].

Conductance Measurements and Thermal Studies

The molar conductance values, measured in EtOH solutions (*ca.* 1×10^{-3} M) for the mononuclear complexes are in the 2.4–18.2 $\Omega^{-1}\,cm^2\,mol^{-1}$ range, showing that the complexes are not electrolytes [31] (Table I).

The metal content was determined by FAAS. The TGA curves for the ligand and its complexes were obtained at a heating rate of 10°C/min in a nitrogen atmosphere

TABLE I Magnetic moment, molar conductance and electronic spectral data of the ligand and the complexes

Compound	μ_{eff}/*atom* (BM)	Λ_M $(\Omega^{-1}\,cm^2\,mol^{-1})^a$	λ_{max} $(nm)^a$
LH_2	–	2.7	290
$[Co(LH)_2(H_2O)_2]$	4.60	3.9	570, 420, 354, 281
$[Ni(LH)_2]$	dia	9.3	682, 478, 355, 294
$[Cu(LH)_2]$	1.68	2.4	629, 430, 365, 300
$[Zn(LH)(Cl)(H_2O)]$	dia	18.2	435, 352, 285, 275

[a] In EtOH.

over the temperature range 20–750°C. The decomposition temperature and the weight losses of the complexes were calculated from the TGA data. The complexes are stable to 123–180°C, and the decomposition of complexes is completed around 603–709°C. All the complexes undergo complete decomposition to the corresponding thermodynamically stable metal oxides, CoO (residue: 11.02%), NiO (residue: 10.96%), CuO (residue: 12.99%) and ZnO (residue: 20.16%). In addition, the thermal stability of all complexes increases in the order: Ni < Cu < Co < Zn [15,32].

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References

[1] L. Tschugaff, *Chem. Ber.* **40**, 3498 (1907).
[2] A. Chakravorty, *Coord. Chem. Rev.* **13**, 1 (1974).
[3] G.N. Schrauzer and J. Kohnle, *Chem. Ber.* **97**, 3056 (1964).
[4] J.V. Burokovich, A.M. Lore and G.P. Vollp, *J. Coord. Chem.* **36**, 1 (1971).
[5] H. Kamogava, Y. Haramoto, T. Nakazowa, H. Sugiura and M. Nanasawa, *Bull. Chem. Soc. Jpn.* **54**, 1577 (1981).
[6] K. Oguchi, K. Sanui and N. Ogata, *Polymer Eng. Sci.* **30**, 449 (1990).
[7] İ. Karataş and H.İ. Uçan, *Synth. React. Inorg. Met.-Org. Chem.* **28**, 383 (1998).
[8] B. Mercimek, M.A. Özler, G. İrez and Ö. Bekaroğlu, *Synth. React. Inorg. Met-Org. Chem.* **29**, 513 (1999).
[9] O. Piloty and H. Steinbock, *Chem. Ber.* **35**, 3113 (1902).
[10] Y. Gök and H. Kantekin, *Polyhedron* **16**, 2413 (1997).
[11] S. Serin and Ö. Bekaroğlu, *Z. Anorg. Allgem. Chem.* **496**, 192 (1983).
[12] E. Taş, A. Çukurovalı and M. Kaya, *J. Coord. Chem.* **46**, 479 (1999).
[13] E. Canpolat, M. Kaya, and A.O. Görgülü, *Polish J. Chem.* **76**, 687 (2002).
[14] E. Canpolat and M. Kaya, *J. Coord. Chem.* **55**, 961 (2002).
[15] O. Güngör, E. Canpolat and M. Kaya, *Polish J. Chem.* **77**, 403 (2003).
[16] E. Canpolat and M. Kaya, *J. Coord. Chem.* **55**, 1419 (2002).
[17] H. Brintzinger and R. Titzmann, *Chem. Ber.* **85**, 344 (1952).
[18] L.J. Kirschenbaum, R.K. Panda, E.T. Borish and E. Mentasti, *Inorg. Chem.* **28**, 3623 (1989).
[19] R.M. Silverstein, G.C. Bassler and T.C. Morril, Spectrometric Identification of Organic Compounds (John Wiley & Sons, New York, 1991), 5th Edn.
[20] A. Gerli and L.G. Marzilli, *Inorg. Chem.* **31**, 1152 (1992).
[21] J.E. Caton and C.V. Banks, *Inorg. Chem.* **6**, 1670 (1967).
[22] E. Taş, A. Çukurovalı and M. Kaya, *J. Coord. Chem.* **48**, 411 (1999).
[23] Y. Gök and E. Özcan, *Transition Met. Chem.* **16**, 393 (1991).
[24] G.E. Efe and E.O. Schlemper, *Polyhedron* **11**(19), 2447 (1992).
[25] T.W. Thomas and A.E. Underhil, *Chem. Soc. Rev.* **1**, 99 (1972).
[26] G.A. Nicholson, J.L. Petersen and B.J. McCormick, *Inorg. Chem.* **21**(9), 3274 (1982).
[27] D.H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry (McGraw-Hill, London, 1989), 4th Edn.
[28] Y. Nishida, K. Hayashida, A. Sumita and S. Kida, *Inorg. Chim. Acta* **31**, 19 (1978).
[29] N.V. Thakkar, R.M. Patil, *Synth. React. Inorg. Met.-Org. Chem.* **30**, 1159 (2000).
[30] V. Ruiz, F. Lloret, M. Julve, J. Faus, M.C. Munoz and X. Solans, *Inorg. Chim. Acta* **213**, 261 (1993).
[31] W.J. Geary, *Coord. Chem. Rev.* **7**, 81 (1971).
[32] E. Dubler and G. Hanggi, *Thermochim. Acta* **124**, 981 (1994).